



Atmospheric Deposition of Toxic Chemicals to the Great Lakes: A Review of Data through 1994

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Abstract

An update is presented of the atmospheric loadings of 11 organochlorine chemicals, five trace elements and four polynuclear aromatic hydrocarbons (PAHs) to the Great Lakes. Intercomparison of this 1994 estimate is made with earlier loading estimates made in 1988 and 1992 by Strachan and Eisenreich. The flux calculations include wet deposition, dry deposition and two-film vapour transfer across each of the lakes. Of these processes, confidence is highest for wet deposition estimates and lowest for the gas transfer component. This is unfortunate since gas transfer has been estimated to be the most important process for the OC chemicals.

PCBs, dieldrin, HCB, DDE, phenanthrene and pyrene are currently showing net loss from the lakes to the atmosphere via volatilization. *p,p'*-DDT is still being loaded into the lakes from the atmosphere. α - and γ -HCH are near equilibrium with the water bodies and show volatilization in the summer and fall for γ -HCH but net deposition for the rest of the year. Hg assessment for the net loading to Lake Superior is given and points out the importance of each of the atmospheric deposition routes for this trace element. The results taken from the IADN program provide a detailed data set for the interpretation of atmospheric impact on the lakes. Relative assessment in relation to other sources of input is difficult due to sparsity of data in other media of the lakes. Particularly important is the inconsistent intercomparison of air and water concentrations from different years leading to gas transfer estimates which could be dated or incorrect. For chemicals which are showing rapidly changing concentrations in the lakes, the calculation of gaseous mass transfer should be made on the basis of short-term, concurrent measurements in both air and water.

Introduction

Since the mid-1980's, the impact of atmospheric deposition to the Great Lakes has been recognized as being large and, in the case of some past use chemicals, dominant. Strachan and Eisenreich (hereafter referred to as SE, 1988) estimated inputs of wet, dry and gas flux deposition of atmospheric toxics to each of the lakes. They found that up to 96% of the PCB inputs to the lakes is atmospheric in origin. This work had considerable influence in the creation of new monitoring and research programs in the U.S. and Canada. In particular, the 1987 revision to the Great Lakes Water Quality Agreement (GLWQA) called for the creation of an Integrated Atmospheric Deposition Network (IADN) in order to provide regular updates of the atmospheric deposition of toxic chemicals to the Lakes and the comparison of those inputs to other sources. In a recent article, the sampling methodologies and initial results from the IADN program have been described (Gatz et al., 1996). The IADN network was formed in the years between 1988 and 1990. The location of the five master stations for IADN are shown in Figure 1. We give here the first published integrated deposition estimates from this network.

In 1992 and in response to the timetable in the Implementation Plan for IADN (Egar and Adamkus, 1990), Eisenreich and Strachan (hereafter referred to as ES, 1992) revised their estimates of wet and dry loadings to the lakes using data from 1989-1991. This report (the "Mauve Bible" or "Purple Document" as it is variously known) included data for chemicals which were addressed in 1988 but added a number of important species which have large current use. The 1992 report also recognized that seasonal inputs to the lakes are not equal, predominantly because air concentrations for some volatile organochlorines can be several orders of magnitude

larger in summer than winter (Hoff et al., 1992).

Three to five years of analysed air and precipitation data are now available from the IADN program. Clearly, it is time to use those measured results for revised estimation of wet and dry loadings to the Lakes. In addition, considerable progress has been made in determining gas transfer fluxes across the air-water interface in the lakes and it is now possible to revisit the 1988 estimates of the relative importance of the wet, dry and gas transfer processes. To this end, a workshop was held in Windsor, Ontario, in June 1994 to revise the estimates of atmospheric inputs to the lakes. This paper reports the loadings derived from results presented at that workshop.

Annex 15 of the GLWQA calls for the determination of the "relative loadings" in each of the lakes. This requires an assessment of the magnitude of the atmospheric processes in relation to the direct input sources of tributary flows, municipal, industrial and fugitive inputs. The data for these other inputs are sparse. Non-atmospheric sources for Lake Superior have been estimated (Dolan et al, 1993) and the determination of relative loadings will be discussed for this, the uppermost, Great Lake, with respect to mercury, lead and PCBs.

Methodology and Data Sources

The IADN Quality Assurance Program Plan (QAPP; Environment Canada, 1994) defines the method of calculating total loading from the atmosphere to the lakes. In this paper, we will divide the loading equation into two terms. The first, L , is the sum of inputs from the atmosphere: a net atmospheric component of the tributary input, wet deposition, dry deposition and gas absorption at the water surface. In addition, we report a loss term, V , which represents volatilization from the water surface (Environment Canada, 1994; Mackay and Yuen, 1983; Baker

and Eisenreich, 1990; Dolan et al., 1993; Hoff, 1994). The absorption plus V equals the net gas flux required in the QAPP (Environment Canada, 1994).

The terms in equations (1) and (2) are described in the glossary. In this paper, the loading,

$$L = \frac{F_t}{C_p} \frac{C_t}{R_p A_p} + A K_{oL} (1 - \alpha_a) C_a \frac{RT}{H} + A C_a v_d \quad \begin{matrix} [\text{atmospheric tributary}] \\ [\text{wet deposition}] \\ [\text{gas absorption}] \\ [\text{dry deposition}] \end{matrix} \quad (1)$$

$$V = A K_{oL} (1 - \alpha_w) C_w \quad [\text{volatilization}] \quad (2)$$

volatilization and net gas loading terms and their errors are presented separately.

In equation (1), the first term involves the recognition that the tributary flow has inputs which are atmospheric in source (wet and dry deposition to the basin and subsequent flushing into the rivers by runoff). The term α_t is the fraction of the tributary flow which is atmospheric in origin, C_t is the tributary concentration and F_t is the tributary flow.

The next three terms in the loading equation represent the wet, gas absorption and dry deposition inputs to the surface of the lakes. In the 1988 estimates of loadings to the lakes (SE, 1988), the net gas transfer term was estimated for -PCB, -DDT, B(a)P, and mirex. Only the wet and dry terms were calculated in the 1992 update of these inputs (ES, 1992). An additional term, representing the loss from the surface of spray and bubble production of particulates, is mentioned in the IADN QAPP (Environment Canada, 1994). Few results exist to estimate the magnitude of this process in the Great Lakes, and, for this reason, this term will not be treated in

this paper. The inputs to the five terms above are described in the sections to follow.

In this calculation, it is implicit that a single average concentration for each lake is used in each medium (air or water). If there are large spatial gradients in concentration, this may lead to errors in loading estimates. As will be discussed below, for many species the interlake variability in concentration is not large, leading to some confidence in using a single estimator for a given lake. However, for some species (especially the trace elements and polynuclear aromatic hydrocarbons), urban influences at a smaller scale may be important. Quantifying sub-lake scale variability is a major research goal (U.S.E.P.A., 1992). To date, however, the magnitude of the urban influences cannot be compared readily to the lakewide averages for all 11 species studied here.

It should be noted that equation (1) defines *loadings* to be *positive* for inputs into the lakes. Volatilization would then represent a negative loading (a loss). This is the approach taken in SE (1988). This convention will be followed in this paper .

Atmospheric-Tributary Inputs

Loadings to the lakes through the tributary inputs (rivers, connecting channels, municipal outflows) all have a component which is atmospheric in origin. Using estimates of deposition of lead, mercury and PCBs to the Lake Superior watershed, Dolan et al.(1993) estimated that roughly 10% of the material which is wet and dry deposited in the watershed reaches the lakes by fluvial transport. This is a different approach than equation (1) which requires that the tributary loads be known (which they are not). Since the magnitude of net gas transfer to the watershed is not quantified in this procedure, we chose not to include such an uncertain term in the loading estimate in equation (1). However, using the approach of Dolan et al. (1993), it can be easily

estimated. The ratio of land basin to lake area is 1.55 for Lake Superior, 2.04 for Lake Michigan, 2.25 for Lake Huron, 3.04 for Lake Erie, and 3.37 for Lake Ontario (Botts and Krushelnicki, 1987). If the 10% contribution estimate is correct, the basin atmospheric-tributary inputs would represent a 16-34% increase on the wet and dry loads. This will be shown to make little impact on the overall loading figure and is well within the error of those estimates. In future updates of the loadings, details of basinwide deposition may have sufficient information to be examined in greater detail.

Wet Deposition

Of the four factors in equation (1), wet deposition is the most straight-forward. It is simply the volume-weighted mean concentration in precipitation times the precipitation rate and the area of the lake. Precipitation rates and areas are generally well known. Errors in the estimation of precipitation rate are due to fluctuations in the yearly rain rate (expected to be about 10%, Hoff, 1994) and whether the site is upwind or downwind of the lake. Errors in the lake area and watershed are considered negligible in comparison with other errors, particularly those in the concentration.

Concentration determinations for the organics typically vary by 30-40% based on replicate sampling at the IADN site at Point Petre. Recoveries of target compounds, as measured by surrogates pre-spiked on the columns employed for most of the wetfall sampling, were generally better than 75%. Results in this paper have not been corrected for this recovery. Analytical error contributes about half the variability; lack of homogeneity in the precipitation and sampling efficiency differences is suggested as contributing the rest of the imprecision. Since wetfall includes both washout of gas and particle phase components, air mass inhomogeneities in

the column swept out by the falling rain or snow is likely to cause variability. The analytical variability between agencies was lessened by eliminating samples of less than 2L total volume over a two-week period (< 10 mm rain equivalent over 2 week sampling) from the volume-weighted mean concentration determinations for the organics.

Of the trace metals reported here (Pb, As, Se, and Cd), mean levels of Pb and Se are several times their detection limits (Pb $0.2 \mu\text{g/L}$, Se $0.1 \mu\text{g/L}$) and there are few values which are not detected. Cd and As mean concentrations, however, are near or below the detection level (both $0.1 \mu\text{g/L}$) and, thus, there is considerable uncertainty in the significance of the wet loadings of these species. We will address mercury in a separate discussion below.

Dry Deposition

The IADN program attempts to directly measure the particulate component of each toxic chemical in the atmosphere. This measured particulate concentration is $_aC_a$ in equation (1). For many trace elements and for some polynuclear aromatic compounds, the combination of air concentrations and analytical sensitivities is sufficient to accurately measure the atmospheric particulate loading. For other species, especially those which are largely gas phase in the atmosphere (Hg, PCBs and the organohalogen pesticides and herbicides), this sensitivity is not as good.

The following approaches are taken in this paper. The first is to directly assess the dry loading from the measured particulate concentration on high volume filters times a deposition velocity. The second approach recognizes that field measurements of the particulate fraction $_a$ rely on the filter-adsorbent samplers to operationally define the particulate concentration. These estimates are subject to bias from a number of sampling artifacts, including blow-off losses of

organics from particles on the filter, chemical transformations during sampling (especially for PAHs), and adsorption of gas-phase organics by the filter itself.

The second approach involves calculation of the a values from the Junge-Pankow adsorption model (Pankow, 1987):

$$a = \frac{c}{p_L^o c} \quad (3)$$

where a is the particle surface area per unit volume of air (cm^2/cm^3 air), p_L is the liquid-phase saturation vapor pressure as a function of temperature, and c is a parameter which depends on the thermodynamics of the adsorption process. Values for p_L are relatively well established, but uncertainties in the J-P model involve c and a . Values of a have been suggested by Bidleman (1988; see Table 1) for urban, rural, and clean air regimes. Often it is assumed that this parameter can be scaled to total suspended particulate, TSP, but a better approach would be to estimate from the particle size distribution measured over the same sampling period as for the organics.

Here in a check of the assumptions of correct apportionment of particulate fraction, we calculate a from the gas/particle ratio from the IADN sampling data and then relate that ratio to the vapour pressure of the compound at an average seasonal temperature. The particle to gas partition coefficient $K_p = F/A(\text{TSP})$ (F is the filter adsorbed fraction, A is the adsorbent fraction, and TSP is the total suspended particulate concentration) has also been estimated from these data. Eventually, this partitioning will be checked sample by sample using daily partitioning information, but that is beyond the scope of this evaluation. The inputs to the calculations are shown in Table 1.

Figure 2a shows the predicted values of f_a for the organochlorines (diamonds) and PAHs (stars) as a function of their vapour pressure. The Junge-Pankow predictions are compared to field measurements from two previous studies (Baker and Eisenreich, 1990; McVeety and Hites, 1988). Relative to both of those estimates, there appears to be too large a gaseous fraction over Lake Superior for the low vapour pressure PAHs (B(a)P and B(k)F) from the IADN data. For Lakes Erie and Ontario (Figure 2b and 2c), the observed data is more in line with the theory, although the measured B(a)P and B(k)F particulate fractions are still low at Sturgeon Point on Lake Erie. It is useful to note that the Point Petre fractionation by AES is done with a filter/PUF sampler at about a 300 m³ total sample volume and the Lake Superior/Lake Erie results are taken by ISWS with a filter/PUF-XAD-2 sampler at an 815 m³ sample volume. It is possible that some of the difference may be a sampler artifact due to higher filter blow-off rates on the higher volume device.

Figure 2d shows the best-fit lines for various studies compared to the J-P model. Green Bay PAH and Chicago PCB distributions (with TSP scaled to 30 µg m⁻³) are from Cotham and Bidleman(1995). The conclusion that can be drawn from this analysis is that the apportionment of gas to particles measured at the IADN stations is generally consistent with the J-P theory. In the loading estimates of equation (1), the high volume sampler $f_a C_a$ values are used. Because of the possible blow-off artifact, this may underestimate the particulate dry deposition and overestimate the gas loading at Lake Superior and Lake Erie for the heavier PAHs. The gas transfer for these heavier PAHs is itself small due to the low Henry's Law partitioning and Figure 2d would suggest that the particulate dry deposition might be increased by 20-40% for the PAHs.

Dry Deposition Velocity

There is no direct measurement of dry deposition flux made in the IADN monitoring program. Techniques which have been used to measure particle deposition velocities (eddy correlation, eddy accumulation, relaxed eddy accumulation, gradient, and bulk techniques) are difficult to carry out on a routine basis, especially at over-water sites. Deposition estimates can be made using models of deposition as a function of particle size, hygroscopic growth of the aerosol, wind speeds and humidities at the water surface (Slinn and Slinn, 1980).

Such deposition estimates have been reviewed in the past and while no complete consensus has been obtained, a deposition velocity of 0.2 cm s^{-1} was considered a reasonable approximation (SE, 1988; ES, 1992). In order to maintain consistency with previous estimates of loading from this process, loads have again been computed using this assumption.

Recent evidence, however, put a wider range on the expected deposition velocities. Using particle size data obtained with the Noll rotary impactor near Chicago, Holsen et al. (1991) estimated that the deposition velocity of PCBs was 5.0 cm s^{-1} , over an order of magnitude larger than the previously accepted value. This conclusion required considerable material to exist on "giant" particles, those of greater than $30 \mu\text{m}$ in diameter in the atmosphere. This is a problematic conclusion since the samplers used to measure organics and metals in the Great Lakes have various inlet heads (particle maximum sizes of 10 to $>25\mu\text{m}$). These samplers might not sample the particles which are most relevant to this high deposition velocity. It should be noted that such large particles might be more often seen very near urban areas and may be most important in the lower, heavily populated Great Lakes.

On the other end of the spectrum, if one were to assume that the particles containing the organic material were hydrophobic in nature, models (Slinn and Slinn, 1980) predict that the

deposition velocity of sub-micron sized particles would be in the range 0.01 to 0.1 cm s⁻¹ (Hoff and Brice, 1993). This gives a range of possible deposition velocities ranging over two orders of magnitude. Using dichotomous sampler results from the U.S. IADN trace metals sampling, we have estimated that the small particle to large particle mass ratio is about 1.5:1 whereas Hoffman et al. (1988) have quoted a 1.9:1 fine/coarse dichotomous sampler mass ratio for suburban areas. Assuming that the small particles have a size of about 0.5 µm and the large particles have a size of 5 µm (Milford and Davidson, 1985), one gets an effective deposition velocity from (Slinn and Slinn, 1980) of 0.2 cm s⁻¹. We will use that value throughout this study although given the large imprecision (which we tentatively estimate to be 100% here and is subject to scepticism from both reviewers of this paper), further work in this area is desperately needed.

Gas Transfer

The third term in equation (1) and equation (2) predicts that the gas flux across the lake surface is a balance between volatilization from and absorption to the water surface, and is controlled by Henry's Law, the concentration gradient, and an overall mass transfer velocity, K_{oL} (Mackay and Yuen, 1983, Schwarzenbach et al., 1993):

$$\frac{1}{K_{oL}} = \frac{1}{k_w} + \frac{RT}{Hk_a} \quad (4)$$

Here the water-side mass transfer coefficient, k_w follows Bidleman and McConnell (1995), Wanninkhof et al. (1991), Hornbuckle et al. (1994, 1995), Schwarzenbach et al. (1993):

$$k_{w,CO_2} = 0.45 u_{10}^{1.64} ; \quad k_{w,x} = k_{w,CO_2} \left(\frac{Sc_x}{Sc_{CO_2}} \right)^{0.5} \quad (5)$$

.where u_{10} is the 10m wind speed, $k_{w,x}$ is the water mass transfer coefficient of chemical x or CO_2 and is scaled by the ratio of water-side Schmidt numbers referenced to CO_2 .

The air-side mass transfer coefficient, for chemical x, $k_{a,x}$, is calculated as in Bidleman and McConnell (1995) and Schwarzenbach et al. (1993):

$$k_{a,H_2O} = 0.2 u_{10}^{0.3} ; \quad k_{a,x} = k_{a,H_2O} \left(\frac{D_{a,x}}{D_{a,H_2O}} \right)^{0.61} \quad (6)$$

where $D_{a,x}$ is diffusivity of the chemical in air. A number of recent intensive studies have shown that the gas flux is strongly seasonally dependent and individual chemicals may show volatilization behavior in the summer and deposition in the winter (McConnell et al., 1992; Hornbuckle et al., 1995; Ridal et al., 1996). High frequency simultaneous sampling of the water and air columns over the lake are obviously to be preferred over seasonal averages of concentrations and temperatures.

Practically in this work, the temperature dependent Henry's Law coefficient for the species studied was taken from experimental sources where available. In general, however, measurements of Henry's Law have been made only at one temperature and adjusted to ambient conditions. The inputs to the Henry's Law calculation are shown in Table 2 .

Seasonal water temperatures (Table 3) were taken from the lakewide surface water

temperatures from satellite remote sensing (Hornbuckle et al., 1995; Mayewska, private communication). The air temperature at the surface is assumed to be equal to the water temperature.

Mass transfer is wind speed dependent. From averages of wind speed at the Point Petre, Ontario, station, the mean annual wind speed is 5 m s^{-1} . At Eagle Harbor, Michigan, the average wind speed is lower (3 m s^{-1}) but this is believed to be suppressed from the wind speed over the water due to trees protecting the anemometer at the site. The overall error in the seasonal average mass transfer velocity due to the wind speed variance is about 50%. Seasonal values from the mass transfer calculation were used in this study and the winter and summer values are shown in Table 4 to illustrate differences in the parameters with season.

The error budget for this term of the net transfer equation can be large (Hoff, 1994). Error in the Henry's Law coefficient is assumed here to be 30% for all species, which encompasses literature values for H for PCBs. Error in the seasonally-averaged mass transfer coefficient was evaluated to be 50% with most of that error due the wind speed RMS variation of about 30% and the non-linearity of k_w with wind speed. Relative standard deviations of the air concentrations for most of the OC species are typically 60-90% and are due to true fluctuations in the seasonal and annual air concentrations, rather than the precision of the measurement which is more typically 20-40% (Gatz et al., 1996). The latter estimate has been made from intraagency replicate sampling which puts the OC, PAH and metal accuracy at about 15-25% and the PCB replication at about 40% (Hoff and Brice, 1993). Intercomparison between agencies in round-robin studies (Cussion, 1992, 1993, 1994) is similar to the intraagency results for OCs, PCBs, and metals. PAH relative standard deviations between laboratories ranged from 12-48% depending

on the chemical but generally fell in the range 15-30% between laboratories. Relative standard deviations of the water concentration are less well known, but water concentrations are much less variable than air concentrations. Intercomparison of sources would lead the authors to place that error at no more than 30%.

The combination of these error terms leads to errors in the absorption term of 60-300% (typically better than 100%) and 50-130% in the volatilization term. The error in the net gas fluxes of the OCs is 50-7400%. The relative errors in the net flux are particularly bad when the chemical is near equilibrium and net gas flux term involves the subtraction of two large, but nearly equal terms. This is the case for the HCH isomers, the lighter PAHs, and for PCB44 and 52. For the other species which are further from equilibrium (dieldrin, HCB, PCB18, PCB101, B(k)F and B(a)P) the estimated error in the net gas flux is about 50-100% which is dominated by the 50% error in the mass transfer coefficient.

Clearly missing in this discussion of potential error in gas flux is the use of data which is not stationary in time (Hoff, 1994). If, as we are required to do here, water concentration data from the past literature is compared with more recent air measurements, potentially much larger errors will occur than those calculated by a propagation of error analysis. The authors would prefer to use air and water data which is taken coincidentally in time, but there is no on-going effort to measure seasonal and annual lake water concentrations as IADN does for air.

Data Sources

The primary sources of air and precipitation data for inputs to equations (1) and (2) are the results for the years 1990-1993 of the IADN program. In the first two years of the program, evaluation of inter-agency comparability was the prime effort. Since not all agencies have

concurrent data available at this time, the workshop focussed on the years 1990 -1992 for each of the lakes, with 1992 as the preference year. Some of these results have been published in journals and agency reports (Gatz et al., 1994, 1996; Hoff et al., 1996; Strachan and Burniston, 1994; Chan et al., 1994). Others are reported here for the first time. The concentrations in precipitation, air particulate and gas absorbent traps for four PCB congeners, seven organochlorines, four PAHs, and four trace elements can be found in Table 5. In this table the airborne concentration of the species are given in ng m^{-3} , precipitation is in ng/L , and the relative standard deviations (in percent) of the results are shown in parentheses. To conserve space, only annual concentrations are given in this table, although seasonal averages are available from the corresponding author and have been used in the loading calculations.

Water concentration data for most of the lakes is sparse and certainly out of proportion to the effort expended in obtaining air concentrations over the lakes. A recent review of Canadian data by L'Italien (1993) was used for dieldrin and the PAHs even though some of the concentrations are dated (1986-1992 timeframe was used). Because of the stale nature of those data, considerable concern about the potential errors in the gas-flux exists and has been noted by reviewers of this paper. A set of water concentration data from a 1992 sampling study on the Lake Guardian (Bicksler and Eisenreich, private communication) has been made available to the authors, which greatly improves the confidence in the gas transfer for the lower Great Lakes. As stated before, the authors would be far more satisfied with concurrent air-water sampling data but no such data exist on a seasonal basis in the water column, except for specific research projects. The inputs used for the calculations are shown in Table 6. In addition, this table shows the calculated equilibrium water concentrations which would yield a net flux of zero in the gas

transfer term of equations (1) and (2) in each of the lakes. If the water concentration in the lakes is greater than this equilibrium concentration, the lakes can be expected to outgas. Since the water concentrations are not as well known as the air concentrations, these values can be used as targets for the sensitivity of water quality concentration observations needed to be useful for gas flux determinations.

Loading Estimates

From concentration data and using equations (1) and (2), it is possible to estimate the dry, wet and gas transfer for each of the Great Lakes across the water surface. These results are shown by season in Table 7. In all the cases shown in the table, the annual value is the sum of the loading of the seasonal values and not from a calculation using annual mean concentration data. Negative values represent loss of the chemical from the lake to the air. Since this paper updates the loading estimates made in SE (1988) and ES (1992), a comparison is made in Table 8.

- HCH and -HCH

Deposition estimates of *- HCH* and *-HCH* should be one of the more precise loading estimates to the Great Lakes given the air-water research studies which have monitored their behavior in the lakes (McConnell et al., 1992; Ridal et al., 1996). While the gas phase measurements of HCH between agencies are in reasonable agreement, the particulate fraction of HCH observed by ISWS at the U.S. sites appears to be much higher than the fraction observed at Point Petre by AES. Resolution of this difference is still being undertaken. This leads to dry deposition loadings of 0.2-1.5 kg y⁻¹ shown in Table 7 for the upper four lakes. These results are a factor of 3-10 higher than in ES (1992). For Lake Ontario, AES results suggest that the dry component of the deposition is <0.2 kg y⁻¹.

The wet deposition loadings of 46-170 kg y⁻¹ are between 0.25 and 1.2 times the results found in ES (1992), but are generally consistent with a downward trend in atmospheric inputs. The higher results for Lake Huron are based on a very limited number of samples for the 1992 sampling season and should be revisited as more data arises. Lake Huron has 3 times the surface area of Lake Ontario and twice the surface area of Lake Erie and this should be borne in mind when comparing the results from these "lower" Great Lakes. The greatest decrease in concentration is for -HCH for the upper Great Lakes showing a factor of four decline in precipitation loading.

The IADN air concentration results here are lower than in McConnell et al. (1992) and are consistent with world-wide decreases seen in HCH concentrations (Bidleman and McConnell, 1995). The net gas loading term of -140 to +1200 kg y⁻¹ is the dominant process for -HCH and -HCH for all the Great Lakes. The -HCH net gas flux is depositional for all lakes. For -HCH over Lake Ontario, wet deposition becomes a comparable input to absorption. In Figure 3a-d, the percentage of the loading for absorption, wet deposition and dry deposition is shown for Lakes Superior, Michigan, Ontario and Erie. These inputs add to 100% and are shown above the zero line. For reference, the volatilization term is shown as a percentage of the load (up to a maximum of 300% of the loading) and for Lakes Michigan and Ontario, the sum of wet deposition and absorption shows the lakes are near an input/output balance for -HCH. For Lakes Superior and Erie for -HCH and for all the Lakes for -HCH, the atmosphere is still loading the water.

In a study in 1990, McConnell et al. (1992) estimated that the annual deposition for -HCH for the lower four lakes would be: Michigan 116, Huron 273, Erie 3, and Ontario 24 kg y⁻¹.

For γ -HCH, they estimated Michigan 98, Huron 105, Erie 32, and Ontario 28 kg y^{-1} . Annually all loadings are positive and depositional. In summer, however, they found that volatilization of γ -HCH occurred in the upper lakes. In a more recent survey, Ridal et al. (1996) estimated a semi-annual (May-October) deposition of 178 kg /6 months for γ -HCH but a volatilization of 90 kg /6 months of γ -HCH. In Figure 3, the γ -HCH and δ -HCH seasonal net gas loadings are shown for Lake Ontario. Ridal's recent results are shown as well for samples taken during the 1993 cruises. While there is difference in magnitude of these results from different years, the direction of the fluxes found here and those of Ridal's are identical in sign, except for the nearly zero Fall γ -HCH results. The estimated error in the seasonal results here vary between 170-410% on a net flux basis and the agreement between the two estimates is within that factor.

In summary for HCH, dry deposition seems to be unimportant, wet deposition contributions are relatively uniform across the five lakes, and gas flux appears to be variable and very important. In general, the lakes (except for γ -HCH in Lake Michigan and Lake Ontario) are not saturated with respect to HCH and for both species, the lakes continue to experience a net loading from the atmosphere.

Dieldrin

Wet deposition of dieldrin (10-58 kg y^{-1}) appears to be far more important than calculated in ES(1992) (over a factor of 10 higher). These results are based on precipitation monitoring by three agencies (ISWS on all lakes except Huron, NWRI on Huron and Ontario, and IWD on Lake Ontario). These results are consistent with a recent study by Chan (1994). Dry deposition is also 3-7 times higher here (1.7-8.0 kg y^{-1}). The net gas loading (-320 to -780 kg y^{-1}) is the dominant transfer mechanism for dieldrin being 5 to 10 times larger than the wet deposition loading (Figure

3). It appears that dieldrin is outgassing from the lakes (volatilization is 5.9, 6.7, and 6.6 times the loading for Lakes Superior, Erie and Ontario). It should be noted, however, that the water concentrations of dieldrin show a decrease from 1986 to 1990 (L'Italien, 1993). This may result from the 1986 water concentrations being taken on whole water samples whereas the 1990 results are "dissolved" concentrations. Comparison of 1992 air data with 1990 water data is also tenuous. If the water concentrations prove to be similar to the 1990 results, a conclusion which can be drawn is that the lakes are a source of dieldrin to the air in the basin. The variation of dieldrin wet and dry deposition among the lakes is proportional to lake size and dieldrin deposition appears to be nearly uniform across the basin when compared on an areal basis. In data from the Pelee Island site used by Chan et al. since 1986 (1994), Lake Erie has about a threefold higher wet loading of dieldrin than Superior or Ontario.

DDE, DDT, DDD

Wet deposition of these three past-use organochlorines is comparable to the results in 1992 (ES, 1992) (see Table 8). Dry deposition is about the same as in 1992 (ES, 1992) for Lakes Michigan and Superior, but about a factor of four larger for the lower lakes (although still minor).

Gas flux estimates can be made using Bicksler and Eisenreich's water concentrations (private communication) and for all the lakes for which both air and water concentrations are available, the flux is now depositional (13-67 kg yr⁻¹). Absorption estimates for the lakes for the DDT species dominate the gas flux and are in the range 10-72 kg yr⁻¹. In SE (1988), the estimates of total-DDT volatilization were 677, 470, 492, 206, and 160 kg yr⁻¹ for the five lakes. This is opposite to the conclusion here.

For Lake Ontario, L'Italien's (1993) DDE concentration in water causes a volatilization

of -180 kg/yr. It is difficult to understand why DDE and DDT should have such different behaviour in Lake Ontario and reiterates the concern about the use of more current air data and with historical water data.

HCB

In general, HCB wet and dry loadings are comparable to those found in 1992 (ES,1994). Wet fluxes are at least 5 times larger than the dry fluxes. This should be expected from the gas-particle predictions of the Junge-Pankow theory (Pankow, 1987), from the high Henry's law constant for HCB (see Tables 2 and 4), and experimental work (Lane et al.,1990). An exception to the agreement with the 1992 data is a six-fold increase in the wet deposition estimate for HCB to Lake Ontario. In ES(1992), C_p was held constant for all the lakes and this appears to be incorrect.

However, these loadings are less important than the gas flux of HCB. Using Bicksler and Eisenreich's 1992 cruise results for the water concentrations, HCB appears to be in near equilibrium but slightly loading the two upper lakes, Superior and Michigan, and volatilizing out of the lower lakes (Erie and Ontario).

PCBs

In an attempt to estimate fluxes for PCB congeners which have a wide range of physico-chemical properties, four PCB congeners (ranging from 3 to 5 chlorines) were studied in detail in this work, PCB18, 44, 52, and 101. For each of these congeners, the Henry's Law constant and the estimated mass transfer velocities are known with greater accuracy than is possible for the sum of the PCBs. The results (Figure 3) show that the flux of PCBs is dominated by the loss of PCBs to the atmosphere. This result is consistent with the findings of other studies (Baker and

Eisenreich, 1990; Hornbuckle et al., 1994, 1995; Baker et al, 1993).

From Table 8, it is apparent that the estimate of PCB wet and dry deposition appears to be getting smaller. Between the 1992 and 1994 estimates, only slight and non-systematic differences occur. Dry deposition estimates of Σ -PCB are nearly the same for Lakes Superior,

Michigan, and Ontario as in ES(1992). For Lake Erie the dry deposition estimate is 60% higher than in ES(1992) and may be due to the proximity of the Sturgeon Point site to urban areas.

The gas flux of PCBs is out of the lakes for all seasons of the year. The net gas transfer loading of -1700 kg y^{-1} for Lake Superior is at the upper limit of the estimates of Baker et al. (1993). When wet and dry deposition are included, the results (Table 8) for Lake Superior are similar to the 1988 predictions in SE(1988). For the lower lakes, the volatilization has been reduced by nearly of factor of two since 1988. Mackay et al. (1994) have examined the PCB fluxes for Lake Ontario using a rate constant model and concluded that 107 kg yr^{-1} enter the lake from the atmosphere and 251 kg yr^{-1} are volatilized out of the lakes. This is about a factor of two less than the $L = 190 \text{ kg yr}^{-1}$ and $V = -440 \text{ kg yr}^{-1}$ found here, but again is within the error estimate limits.

Particulate Trace Elements (Pb, As, Se, Cd)

For each of these species, there is assumed to be a negligible gas phase component. The Pb wet deposition shows decreases of 4-56% from ES(1992) (except for Lake Huron which has a 9% increase) and this is expected to be due primarily to decreasing concentrations of Pb with time (Reid et al., 1993). Pb shows a slight increase in dry deposition over 1992 (ES, 1992) ($4.5\text{-}18 \text{ T y}^{-1}$ versus $4.5\text{-}13 \text{ T y}^{-1}$). Lake Superior shows greatly increased dry deposition over the 1992 estimate and this is due to a choice of lead air concentration of 1 ng m^{-3} in 1992 near this

uppermost Great Lake, a choice which appears to have been too small.

As and Cd dry deposition, however, is significantly lower (factors of 2 and 5) than the 1992 result (ES, 1992) and this is due to improved averages in the particulate air concentration of these species. Figure 3 shows the wet/dry percentages of the loading and points out that, with a 0.2 cm s^{-1} dry deposition velocity, wet deposition of trace metals dominates the loading estimate.

Mercury (Hg)

Among the toxic trace elements considered here, mercury is unique because it exists in the atmosphere predominantly in the vapor phase. Due to its volatility, unlike the other trace metals, Hg must be treated similarly to a predominantly vapor phase SOC, such as HCH or HCB, when estimating atmospheric inputs and air-water exchange fluxes.

Because of the difficulties in the routine collection and analysis of Hg in environmental samples, this metal was not included in the IADN target list of compounds, but was directed at the research phase of the Great Lakes program. Information on the Hg concentrations in air is currently sparse. A high-quality data set of multi-media mercury concentrations in central Wisconsin now exists (Fitzgerald, et al., 1991; Watras et al., 1991). A more limited data set from the IADN site at Point Petre and at Egbert, Ontario, have been published (Schroeder and Markes, 1994). Estimates of mercury deposition have also been made by Dolan et al. (1993) for Lake Superior and we will reexamine those results here.

Table 9 summarizes the concentrations of Hg associated with various types of environmental samples, as reported by Fitzgerald and co-workers at Little Rock Lake, WI between May 1988 and August 1990 (Fitzgerald et al, 1991). Because of the relatively remote location of the study site, these results should be applicable to the concentrations over Lake

Superior. They considered total gaseous mercury and particulate mercury in the atmospheric compartment. We consider here separately two other Hg species found in Great Lakes air: gaseous elemental mercury, Hg(0), and gaseous divalent mercury, Hg(II), as well as the particulate phase mercury, Hg_p (Schroeder and Markes, 1994; Bloxam et al., 1991; Petersen et al., 1995).

Using the concentration values in Table 9, it is possible to determine the annual atmospheric loading of Hg to Lake Superior and its drainage basin using equations (1) and (2). For the atmospherically derived tributary portion of the load, we have used 10% of the monitored tributary, unmonitored tributary and direct runoff values found in Dolan et al. (1993). This term amounts to $\sim 15 \text{ kg Hg y}^{-1}$. The remaining terms are shown in Table 10. The gas absorption at the water surface is 65 kg y^{-1} and the volatilization of Hg(0) from the surface is 240 kg y^{-1} . Thus, on an annual basis a net transfer of 175 kg Hg y^{-1} takes place from Lake Superior's surface waters to the atmosphere. This is about 20% of the total (wet plus dry) Hg deposition to the lake and emphasizes the importance of including the gas-transfer process in the mass balance.

From the results in Table 10, it is evident that our estimates for the wet and dry deposition of Hg to this lake are significantly smaller than the values found in ES (1992), but are close to the values found in Dolan et al. (1993). The total deposition of 810 kg y^{-1} (wet plus dry) is in excellent agreement with an estimate of 820 kg y^{-1} derived by Knauer (personal communication, 1994).

PAHs

The four PAH species reported here, phenanthrene (Phen), pyrene (Pyr), benzo(k)fluoranthene (B(k)F) and benzo(a)pyrene (B(a)P), have very different physical and

chemical properties. The lower molecular weight PAHs have an appreciable gas phase component while B(a)P is predominantly found on particles at all environmental temperatures.

As mentioned in the section on dry deposition above, there is some discrepancy in the IADN data between gas phase B(k)F and B(a)P on the adsorbent traps used by ISWS and AES. ISWS finds considerably higher gas phase PAH concentrations than does AES for the higher molecular weight PAHs and this needs to be resolved. As a result B(k)F and B(a)P have markedly different gas phase behavior between the upper lakes (measured by ISWS) and Lake Ontario (where the AES data was used).

Wet loadings for the four PAH species are somewhat scattered in relation to the 1992 results (ES 1992; see Table 8). Benzo(a)pyrene appears to be systematically higher in the present results and this is probably due to an underestimate in the B(a)P concentration in ES(1992). This particulate underestimate is severe for dry deposition where the results here are about a factor of ten higher than in ES(1992) for all species except B(k)F.

The observation of a significant gas flux for all of the PAH species needs to be emphasized here (Figure 3). While, as discussed earlier, there is evidence from the gas particle partitioning estimates that the Lake Superior, Michigan, and Erie absorption values may be overestimated at the expense of the dry deposition flux. The comparison of panels 2a, 2b and 2d versus 2c would indicate this. There is still a detectable gas flux of B(k)F from Lake Ontario if the water concentration estimates of L'Italien (1993) are correct.

Relative Loadings to the Lakes

As mentioned in the introduction, one of the prime purposes of the GLWQA Annex 15 activities (of which IADN is a part) is the determination of the relative magnitude of the

atmospheric loading in relation to other inputs. For the species given here, those other inputs are often not quantified. A recent IJC report Dolan et al.(1993) has quantified many of these other inputs for Lake Superior. For Pb, Dolan et al. computed non-atmospheric loading of 23000 kg y⁻¹ plus 7000 kg y⁻¹ of direct runoff (including an atmospheric component). With the 54000 kg y⁻¹ estimated here for wet plus dry deposition, Pb would be 64% atmospheric in loading on Lake Superior (compared to 70% as found in Dolan et al. (1993)).

For -PCBs, Dolan et al.(1993) estimated that 52 kg per year entered the Lake Superior from direct, non-atmospheric inputs plus 18 kg y⁻¹ from direct runoff (including atmospheric). Wet and dry deposition were estimated at 156 kg y⁻¹ (here we find 85 kg y⁻¹). Absorption was estimated at 137 kg y⁻¹ (here we find 320 kg y⁻¹ but estimate 110% error in that number). Including volatilization, tributary inflow and runoff (65 kg y⁻¹) and outflow (43 ky y⁻¹; ES, 1988) , however, we calculate that the lake should be losing 1600 kg y⁻¹. Net removal at the bottom of the lake is not included in this estimate, but has been indicated to be of order 50 kg y⁻¹ (Baker et al., 1993). This indicates that Lake Superior is being purged of PCBs at a rate which is about 21%/year of its burden of 7200 kg (Baker et al., 1993). This process is 34 times more significant than sediment removal at the bottom of the lake. A process this efficient would be expected to rapidly lower water concentrations in the lakes, and Jeriamiason et al. (1995) conclude that a decrease in water concentration of 0.2 yr⁻¹ is occurring.

Conclusions

Updated estimates of the loadings of PCBs, 11 OC compounds, five trace elements, and four PAHs have been made for the five Great Lakes, using data primarily from the IADN network. The results provide improved estimates of the loadings on a seasonal basis to each of

the lakes from previous estimates made by Strachan and Eisenreich (1988) and Eisenreich and Strachan (1992). In particular, the inclusion of a gas transfer term in the loading equation makes it clear that this process cannot be neglected in atmospheric loading assessments. The data for dieldrin, -HCH, HCB and PCBs show that the fluxes are dominated by gas transfer. For the lower molecular weight PAHs, phenanthrene and pyrene, and for Hg, the gas transfer term is as significant as wet and dry deposition. For DDT, there is indication that the gas term can be greater than the wet deposition flux, yet poor resolution of lakewide water concentrations make the determination of the gas flux tenuous at best. Clearly, integrated air-water assessments of the gas term are needed on each lake.

The workshop pointed out the need for further reliable estimates of Henry's law coefficients, deposition velocities, and loadings from other sources. Estimates of the physical and chemical properties of many of these chemicals have come a long way since 1988 and their current precision may be sufficient when taken in balance with the lack of water concentration data. It appears that fluctuations in air and precipitation concentrations are not the controlling factor in the accuracy of the overall loading estimates of these species at this time. It is difficult to make relative loading assessments when other input sources to the lakes are poorly quantitated.

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It is unfortunate that one of the contributors to the workshop passed away during the summer of 1994. As a co-author with Steve Eisenreich to "The Plan" (the original blue-print for the IADN effort on Great Lakes research), Eva Voldner gave years of personal commitment to understanding the health of these largest of freshwater lakes. She is greatly missed by her colleagues and this work is dedicated to her memory and her vision.

Glossary (units represent those used in the flux calculation)

A	Area of lake (m^2)
A_p	Area of lake covered by precipitation (m^2)
c	J-P "constant" (cm Pa)
C_a	Concentration in air (ng m^{-3})
C_p	Concentration in precipitation ($\mu\text{g l}^{-1}$)
C_w	Concentration in water ($\mu\text{g l}^{-1}$)
C_t	Concentration in tributary ($\mu\text{g l}^{-1}$)
$D_{a,x}$	diffusivity ($\text{cm}^2 \text{s}^{-1}$)
F	Resuspension flux function ($10^3 \text{ m}^3 \text{ yr}^{-1}$)
F_t	Tributary flow ($10^3 \text{ m}^3 \text{ yr}^{-1}$)
H	Henry's law coefficient ($\text{Pa m}^3 \text{ mol}^{-1}$)
K_p	particle to gas partition coefficient
K_{oL}	Air-water mass transfer coefficient (m yr^{-1} in eq.1,2, m d^{-1} in eq. 4)
$k_{w,x}$	water-side mass transfer coefficient (m d^{-1}) of the gas x
$k_{a,x}$	air-side mass transfer coefficient (m d^{-1}) of the gas x
L	Loading of chemical to lake (g yr^{-1})
p_L^o	liquid phase saturation vapour pressure (Pa)
R	Gas constant ($\text{Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$)
R_p	Rate of precipitation (m yr^{-1})
Sc_x	Schmidt number of the gas x in water
T	Ambient temperature (K)
u	Mean wind speed (m s^{-1})
u_{10}	Wind speed at 10 m height (m s^{-1})
v_d	Particulate deposition velocity (m yr^{-1})
V	Volatilization flux (kg yr^{-1})
	particle surface area per unit volume (cm^{-1})
a	Particulate fraction of the concentration in air
w	Particulate fraction of the concentration in water
t	Fraction of tributary loading which is atmospheric in origin

Figure Captions

- Figure 1: Map of the Great Lakes with the locations of the five IADN Master Stations
- Figure 2: a) Experimental determination of the particle fraction, f_p , from the Eagle Harbor (ISWS) site on Lake Superior plotted against the logarithm of the sub-cooled liquid vapour pressure. The stars represent the four PAH species for four seasons, and the diamonds represent the OCs. The solid line is from the theory of Junge-Pankow (1987) and the dotted lines are best fit data of Baker and Eisenreich (1990) and McVeety and Hites (1984).
 (b) As for (a), for ISWS sampling at Sturgeon Point on Lake Erie,
 (c) As for (a), for AES sampling at Point Petre,
 (d) A synthesis of IADN partition data for OCs and PAHs at Point Petre and Sturgeon Point (PP-SP) versus the Junge-Pankow prediction (J-P) and Cotham's results in Green Bay and Chicago.
- Figure 3a-d Fraction of the loading which is due to absorption, wet deposition, and dry deposition for Lakes Superior (a), Michigan (b), Ontario (c), and Erie (d). These fractions add to 100%. Also shown is the volatilization /loading ratio to a maximum of 300%. Values which have overrun the graph are noted by arrows. An asterisk (*) indicates that insufficient water concentration data exists to make an estimate of volatilization.
- Figure 4: Seasonal net gas flux for CH_4 and HCH . The CH_4 values are positive and depositional in the summer while the HCH values are negative (volatilizational) in the summer and fall months. Also shown as labels are 1993 estimates for these seasons from Ridal et al. (1996).

Table 1: Inputs to the calculation of .

Lake	Temperature (C)				TSP	*
	Winter	Spring	Summer	Fall	$\mu\text{g m}^{-3}$	$\text{cm}^2 \text{cm}^{-3}$
Superior	-10	2	16	6	10	4.2×10^{-7}
Erie/Ont.	-1	7	21	10	30	1.5×10^{-6}

*The -values correspond to clean and average continental background conditions (Bidleman, 1988).

Table 2. Henry's Law ($\text{pa m}^3 \text{mol}^{-1}$) Values Used
(of the form $H(T) = H(T_r) \exp [m (1/T_r - 1/T)]$)

Chemical	T _r	H(T _r)	Ref.	m	Ref.
-HCH	298	0.76	a	-6471	a
-HCH	298	0.35	a	-5485	a
Dieldrin	298	5.9	b	-7868	c
DDT	296	1.2	d	-7868	c
DDD	298	0.64	e	-7868	c
HCB	293	41	f	-5900	f
PCB18	293	29.6	g	-6000	f
PCB44	293	18.7	g	-6000	f
PCB52	293	16.4	f	-6260	f
PCB101	293	17.6	g	-6260	f
PCBs	293	20	g	-6000	f
Phenan.	298	3.9	h	-6900	f (by similar comp.)
Pyrene 298	1.5	i	-6900	f (by similar comp.)	
B(k)F	293	0.051	f	-5900	f
B(a)P	293	0.034	f	-4700	f

Refs: a) Kucklick et al. (1991); b) Warner et al. (1987); c) Tateya et al. (1988); d) Fendinger et al. (1989); Suntio et al. (1987); f) ten Hulsher et al. (1992); g) Murphy et al. (1987); h) Mackay et al. (1979); i) Mackay and Shiu (1981)

Table 3: Lake Surface Temperatures (K)
Lake Michigan data from Hornbuckle et al. (1995); all others from Mayewska (1994)

Lake	Winter	Spring	Summer	Fall	Annual
Superior	275.0	274.2	282.1	282.3	278.4
Michigan	274.0	275.0	288.0	284.0	280.0
Huron	275.5	275.2	287.4	285.0	280.8
Erie	275.0	278.0	292.9	288.4	283.6
Ontario	275.9	276.1	290.0	285.3	281.8

Table 4: Mass Transfer Calculation Results

Species	Seas	Lake Superior					Lake Michigan				Lake Erie				Lake Ontario			
		Ka	H	Sc	Kw	KoL	H	Sc	Kw	KoL	H	Sc	Kw	KoL	H	Sc	Kw	KoL
		(m/d)	(pa m ³ mol ⁻¹)		(m/d)	(m/d)	(pa m ³ mol ⁻¹)		(m/d)	(m/d)	(pa m ³ mol ⁻¹)		(m/d)	(m/d)	(pa m ³ mol ⁻¹)		(m/d)	(m/d)
-HCH	W	402	1.24e-01	4917	0.53	0.021	1.13e-01	5296	0.51	0.019	1.24e-01	4917	0.53	0.021	1.33e-01	4612	0.55	0.022
	Su		2.23e-01	3132	0.66	0.036	3.57e-01	2188	0.79	0.056	5.20e-01	1655	0.91	0.078	4.17e-01	1950	0.84	0.064
-HCH	W	402	7.55e-02	4917	0.53	0.013	7.02e-02	5296	0.51	0.012	7.55e-02	4917	0.53	0.013	8.06e-02	4612	0.55	0.014
	Su		1.25e-01	3132	0.66	0.021	1.86e-01	2188	0.79	0.030	2.56e-01	1655	0.91	0.040	2.12e-01	1950	0.84	0.034
Diedrin	W	357	6.48e-01	6130	0.47	0.084	5.84e-01	6602	0.46	0.076	6.48e-01	6130	0.47	0.084	7.12e-01	5749	0.49	0.090
	Su		1.33e+00	3905	0.59	0.151	2.36e+00	2728	0.71	0.235	3.73e+00	2064	0.82	0.327	2.85e+00	2431	0.75	0.270
DDE	W	365	4.47e+00	5938	0.48	0.287	4.02e+00	6396	0.46	0.270	4.47e+00	5938	0.48	0.287	4.90e+00	5569	0.50	0.303
	Su		9.18e+00	3783	0.60	0.424	1.62e+01	2642	0.72	0.558	2.57e+01	1999	0.83	0.682	1.96e+01	2355	0.76	0.607
DDT	W	356	1.58e-01	6203	0.47	0.023	1.42e-01	6681	0.45	0.021	1.58e-01	6203	0.47	0.023	1.73e-01	5818	0.49	0.025
	Su		3.24e-01	3952	0.59	0.045	5.73e-01	2760	0.71	0.076	9.06e-01	2088	0.81	0.114	6.92e-01	2460	0.75	0.090
DDD	W	363	7.03e-02	5988	0.48	0.011	6.34e-02	6449	0.46	0.010	7.03e-02	5988	0.48	0.011	7.72e-02	5616	0.49	0.012
	Su		1.45e-01	3814	0.60	0.022	2.56e-01	2664	0.72	0.037	4.04e-01	2016	0.83	0.056	3.09e-01	2375	0.76	0.044
HCB	W	508	1.10e+01	2992	0.68	0.530	1.01e+01	3222	0.65	0.507	1.10e+01	2992	0.68	0.530	1.18e+01	2806	0.70	0.552
	Su		1.88e+01	1906	0.85	0.703	2.89e+01	1331	1.02	0.871	4.07e+02	1007	1.17	1.026	3.33e+01	1187	1.08	0.933
PCB18	W	391	7.75e+00	5227	0.51	0.370	7.15e+00	5630	0.49	0.352	7.75e+00	5227	0.51	0.370	8.32e+00	4903	0.53	0.385
	Su		1.34e+01	3330	0.64	0.499	2.07e+01	2326	0.77	0.626	2.94e+01	1760	0.88	0.744	2.39e+01	2073	0.81	0.673
PCB44	W	381	4.89e+00	5462	0.50	0.311	4.52e+00	5883	0.48	0.295	4.89e+00	5462	0.50	0.311	5.26e+00	5123	0.52	0.325
	Su		8.48e+00	3479	0.63	0.432	1.31e+01	2430	0.75	0.553	1.86e+01	1839	0.86	0.666	1.51e+01	2166	0.80	0.597
PCB52	W	381	4.05e+00	5462	0.50	0.288	3.73e+00	5883	0.48	0.272	4.05e+00	5462	0.50	0.288	4.36e+00	5123	0.52	0.302
	Su		7.18e+00	3479	0.63	0.409	1.13e+01	2430	0.75	0.530	1.63e+01	1839	0.86	0.645	1.31e+01	2166	0.80	0.576
PCB101	W	381	4.35e+00	5690	0.49	0.293	4.00e+00	6129	0.47	0.277	4.35e+00	5690	0.49	0.293	4.68e+00	5337	0.51	0.307
	Su		7.71e+00	3625	0.62	0.413	1.21e+01	2532	0.74	0.533	1.75e+01	1916	0.85	0.647	1.41e+01	2257	0.78	0.578
Sum-PCB	W	373	5.23e+00	5494	0.50	0.315	4.83e+00	5917	0.48	0.299	5.23e+00	5494	0.50	0.315	5.62e+00	5153	0.52	0.330
	Su		9.07e+00	3500	0.63	0.437	1.40e+01	2444	0.75	0.558	1.99e+01	1849	0.86	0.671	1.62e+01	2179	0.79	0.603
PHEN	W	380	5.62e-01	4665	0.54	0.080	5.13e-01	5025	0.52	0.074	5.62e-01	4665	0.54	0.080	6.10e-01	4376	0.56	0.086
	Su		1.06e+00	2972	0.68	0.137	1.75e+00	2076	0.81	0.207	2.61e+00	1571	0.93	0.284	2.06e+00	1850	0.86	0.236
PYR	W	419	2.16e-01	4851	0.53	0.037	1.97e-01	5225	0.51	0.034	2.26e-01	4851	0.53	0.038	2.35e-01	4550	0.55	0.040
	Su		4.07e-01	3090	0.67	0.066	6.71e-01	2159	0.80	0.102	6.39e-01	1633	0.92	0.098	7.92e-01	1924	0.84	0.118
B(k)F	W	409	1.15e-02	5533	0.50	0.002	1.06e-02	5959	0.48	0.002	1.20e-02	5533	0.50	0.002	1.23e-02	5190	0.51	0.002
	Su		1.97e-02	3525	0.62	0.013	3.03e-02	2462	0.75	0.005	2.90e-02	1863	0.86	0.005	3.49e-01	2194	0.79	0.006
B(a)P	W	381	5.86e-03	5533	0.50	0.001	5.28e-03	5959	0.48	0.001	6.18e-03	5533	0.50	0.001	6.44e-03	5190	0.51	0.001
	Su		1.20e-02	3525	0.62	0.002	2.13e-02	2462	0.75	0.003	2.01e-02	1863	0.86	0.003	2.58e-02	2194	0.79	0.004

Table 5: Annual Mean Gas Phase, Particulate Phase and Precipitation Concentration Data from IADN by Lake*

Chemical	Eagle Harbor, MI (Superior)			Sleeping Bear Dunes, MI (Mich)			Burnt Is.	Sturgeon Point, NY (Erie)			Point Petre, ON (Ontario)		
	Gas (pg m ⁻³)	Particulate (pg m ⁻³)	Precip. (ng/l)	Gas (pg m ⁻³)	Particulate (pg m ⁻³)	Precip. (ng/l)	Precip. (ng/l)	Gas (pg m ⁻³)	Particulate (pg m ⁻³)	Precip. (ng/l)	Gas (pg m ⁻³)	Particulate (pg m ⁻³)	Precip. (ng/l)
-HCH	110 (60)	0.22 (55)	1.4 (40)	120 (66)	0.33(76)	1.4 (25)	3.3	160 (73)	0.5 (95)	1.5 (34)	79 (53)		2.8 (28)
-HCH	32 (90)	0.12 (58)	1.23 (50)	210 (232)	0.26(140)	1.6 (35)	2.3	56 (120)	0.2 (120)	1.3 (35)	27 (94)	0.1 (58)	2.5 (36)
Dieldrin	14 (100)	1.5 (23)	0.4 (21)	34 (90)	1.9(41)	0.99 (18)	0.18	30 (100)	3.2 (54)	0.8 (18)	23 (93)	1.6 (65)	0.6 (30)
DDE	2.5 (100)	0.08(63)	0.06 (17)	11 (76)	0.13(38)	0.09 (33)	0.14	18 (110)	0.3 (85)	0.2 (33)	16 (100)	0.1 (65)	0.2 (56)
DDT	3.9 (110)	0.3 (29)	0.2 (38)	9.4 (190)	0.45 (91)	0.47 (36)	0.31	13 (110)	2.2 (100)	1.4 (43)	7.0 (160)	3.6 (100)	0.2 (68)
DDD	1.5 (80)	1.2 (58)	0	3.7 (120)	1.1		0.1	7.7 (110)	1.3 (25)	0.09 (44)	2.3 (150)	1.0 (40)	0.2 (62)
HCB	98 (43)	0.2 (87)	0.1 (30)	120 (26)	0.1	0.06 (16)	0.13	80 (61)	0.2 (86)	0.04 (25)	130 (36)	<0.1	0.3 (55)
PCB18	4.8 (85)	0.05 (20)	0.02 (75)	7.8 (69)	0.05 (20)	0.02 (40)	0.21	20 (87)	0.09 (78)	0.02	9.8 (79)	0.06 (50)	0.2 (60)
PCB44	3.4 (110)	0.1 (33)	0.03 (33)	9.7 (92)	0.09	0.03	0.32	14 (71)	0.2 (65)	0.02	6.6 (84)	0.1 (90)	0.2 (55)
PCB52	4.2 (98)	0.06 (50)	0.02	6.4 (56)	0.06 (33)	0.02	0.12	16 (75)	0.2 (56)	0.02	6.8 (91)	0.06 (75)	0.08 (54)
PCB101	2.3 (96)	0.1 (27)	0.04 (25)	4.0 (63)	0.09 (33)	0.03	0.14	9.8 (74)	0.2 (67)	0.02	3.3 (120)	0.09 (37)	0.1 (57)
- PCB	90 (95)	5.6 (23)	1.2 (19)	160 (61)	4.9 (28)	1.1 (22)	2.5	360 (81)	8.8 (45)	0.7 (18)	170 (86)	4.7 (34)	3.1 (50)
Pb		2500 (88)	700 (175)		4800 (54)	1100 (57)	1400		11000(33)	1700 (116)		3700 (97)	2400 (5)
As		700	200 (89)		500 (100)	100 (42)	100		1100 (55)	200 (97)		480 (63)	200 (5)
Se		300	600 (78)		800 (63)	400 (76)	200		1500 (33)	700 (46)		830 (100)	300 (8)
Cd		500 (100)	250 (79)		300 (100)	200 (110)	100		800 (50)	130 (93)		70 (150)	200 (36)
Phen-	860 (120)	19 (69)	3.7 (16)	920 (69)	26 (66)	5.5 (28)		4000 (68)	60 (77)	11 (34)	760 (94)	37 (120)	3.2 (16)
Pyrene	190 (170)	22 (16)	2.7 (19)	97 (57)	35(48)	4.0 (22)		510 (100)	74 (71)	8.2 (33)	190 (210)	58 (120)	3.4 (17)
B(k)F	19 (34)	22 (16)	2.7 (19)	17 (21)	13 (59)	2.6 (16)		19 (34)	74 (71)	8.2 (33)	2.6 (230)	58 (120)	3.4 (17)
B(a)P	9.3 (23)	11 (47)	2.9 (13)	10 (30)	21 (31)	3.8 (21)		13 (62)	44 (76)	5.1 (20)	3.0(250)	45 (110)	3.0 (17)

* Values in parentheses are the percentage error in the concentrations

Table 6: Water Concentration Data (ng/L) and Equilibrium Water Concentrations (ng/L)

	Superior			Michigan			Huron		Erie			Ontario		
Chemical	Conc. (ng/L)	Ref	Equil. Conc. (ng/L) [#]	Conc. (ng/L)	Ref	Equil. Conc. (ng/L) [#]	Conc. (ng/L)	Ref	Conc. (ng/L)	Ref	Equil. Conc. (ng/L) [#]	Conc. (ng/L)	Ref	Equil. Conc. (ng/L) [#]
a-HCH	1.1	a	1.2-1.9	1.6	a	0.9-2.6	1.5	a	1.1	a	0.83-2.9	0.8-0.9	a	.52-1.1
g-HCH	0.4	a	0.31-1.9	0.34	a	0.68-7.6	0.38	a	0.49	a	.33-2.3	0.36	a	.2 - 1.0
Dieldrin	0.26	b	0.03-0.05			0.04-0.13	0.35	b	0.38	b	.019-.06	0.32	b	.03-.06
pp-DDT	0.007	f	.017-.044	0.005	f	.045-.15	0.002	f	0.002	f	.03-.13	0.004	f	.023-.09
HCB	0.01	f	.012-.021	0.014	f	.011-.027	0.007	f	0.014	f	.004-.016	0.045	f	.004-.014
PCB18	0.011	*	.0006-.0014	.017	c	.001-.0027	0.005	f	0.01	f	.001-.007	0.007	f	.002-.005
PCB44	0.0041	*	.0007-.0017	0.014	c	.0025-.0033	0.002	f	0.006	f	.002-.004	0.007	f	.001-.002
PCB52	0.004	*	.0008-.0020	0.018	c	.0016-.0038	0.002	f	0.008	f	.002-.006	0.009	f	.001-.003
PCB101	.009	*	.0005-.0013	0.0094	c	.0009-.0022	0.0003	f	0.004	f	.001-.003	0.002	f	.0008-.0014
-PCB	0.18	d	.017-.034	0.36	c	.032-.070	0.09	f	0.17	f	.05-.15	0.18	f	.038-.085
PHEN	3.5	e	1.1-4.0			0.9-8.4					1.9-6.6	1.2	b	.32-2.1
PYR	0.28	e	0.45-2.6			0.25-2.3					0.86-2.0	0.45	b	0.17-1.0
B(k)F	0.02	e	1.8-3.4			0.13-3.6					.32-1.3	0.28	b	.01-.35
B(a)P	0.39	e	1.8-3.9			1.1-5.8					2.3-13			.84-2.1

* Indicates that the PCB congener concentration is taken from the congener ratios in Baker and Eisenreich (1990) and using the -PCB concentrations

Equilibrium water concentrations are the range of seasonal values which makes absorption in equation (1) equal to volatilization in equation (2)

Refs: (a) McConnell and Bidleman, 1992, b) L'Italien, 1993, c) Hornbuckle et al., 1995, (d) Jeriamiason et al., 1994; e) Baker and Eisenreich, 1990, f) J. Bicksler and S. Eisenreich, personal communication 1996.

Table 8: Intercomparison of Loading Estimates for the Great Lakes(SE (1988); ES(1992); 1994 here)

Chemical (year)	Superior (kg/yr)	Michigan (kg/yr)	Huron (kg/yr)	Erie (kg/yr)	Ontario (kg/yr)
- PCBs (Wet+Dry)					
1988	550	400	400	180	140
1992	160	110	110	53	42
1994	85	69	180	37	64
- PCBs (Net Gas)					
1988	-1900	-5140	-2560	-1100	-708
1994	-1700	-2700	na	-420	-440
-DDT (Wet + Dry)					
1988	90	64	65	33	26
1992	34	25	25	12	10
1994	17	32	37	46	16
- DDT(Net Gas)					
1988	-681	-480	-495	-213	-162
1994	30	67	na	34	13
B(a)P (Wet and Dry)					
1988	69	180	180	81	62
1992	120	84	84	39	31
1994	200	250	na	240	120
Pb (Wet + Dry)					
1988	230,000	540,000	400,000	230,000	220,000
1992	67,000	26,000	10,000	97,000	48,000
1994	51,000	72,000	100,000	65,000	45,000

Table 9: Concentration of mercury associated with various media (Lake Superior and its Basin)

Sample Type and Concentration					Ref.
Gaseous Hg (0) ng m ⁻³	Gaseous Hg (II) pg m ⁻³	Particulate Hg pg m ⁻³	Precipitation Hg (total) ng L ⁻¹	Lake ^a Water Hg(0) pg L ⁻¹	
1.6 ± 0.4 range: 1.0 - 2.4 (n=48)	ND	22 ±19 range: 7-62 (n=15)	rain: 10.5 ± 4.8 (3.2-15) snow: 6.0 ± 0.9 (5-11)	range: 7-42	Fitzgerald et al. (1991)
2	ND	ND	20	ND	ES (1992)
1.6	3	30	9	25 ^c	This work

ND = not determined or reported

a: near surface water concentration of dissolved gaseous elemental mercury

b: taken as 2.5% of total mercury concentration in lake water.

Table 10: Calculated annual loading of mercury to Lake Superior (kg y⁻¹)

Tributary Input	Wet Deposition	Dry Deposition	Gas Exchange of Hg (0)		Net Gas Transfer
			Absorption	Volatilization	
15 ^a	560 (1250) ^b	250 ^c (930) ^b	65	-240	-175

^a Estimated from values in Dolan et al.(1990) ^b Values in brackets from ES(1992) ^c Includes 155 kg y⁻¹ of particulate Hg and 95 kg y⁻¹ of gaseous Hg(II)